Application of magnetic lamotrigine-imprinted polymer nanoparticles as an electrochemical sensor for trace determination of lamotrigine in biological samples

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Synthesis of Fe_3O_4@SiO_2

For preparation of Fe_3O_4 nanoparticles, 10.4 g of $FeCl_3.6H_2O$ and 4.0 g of $FeCl_2.4H_2O$ were dissolved in 100 mL of deionized water, degassed with nitrogen for 15 min and heated to 80 °C. Then, 15 mL of NH_4OH (32% solution) was added dropwise to the solution. After 15 min the solid was separated by a magnet and washed three times with 0.1 mol L^{-1} NaCl solution [1]. The synthesized Fe_3O_4 nanoparticles (1.0 g) were dispersed in 300 mL mixture of ethanol and double distilled water (4:1, v/v) by ultrasonic vibration for 15 min. Subsequently, NH_4OH (15 mL) and tetraorthosilicate (2.1 mL) were continuously added into the reaction mixture. The reaction was stirred for 12 h at 40 °C and finally the product was collected by a magnet.

Synthesis of Fe3O4@SiO2@MPTS

Fe_3O_4@SiO_2 nanoparticles (500 mg) were chemically modified by 5.0 mL of 3-methacryloxypropyl trimethoxysilane (MPTS) in 30 mL toluene solution under nitrogen atmosphere. The mixture was refluxed for 24 h at 120 °C and then Fe_3O_4@SiO_2@MPTS was collected by a magnet and washed with toluene and distilled water.

Characterization of magnetic molecular imprinted polymer

Figure 1S (Electronic Supplementary Material (ESM)) shows the XRD patterns of the Fe_3O_4, Fe_3O_4@SiO_2, Fe_3O_4@SiO_2@MPTS and MMIPs magnetic nanoparticles. There are several relatively strong diffraction peaks in the region of 20–70, which are identical to those of Fe_3O_4 nanoparticles reported earlier [2,3]. This revealed that Fe_3O_4, Fe_3O_4@SiO_2, Fe_3O_4@SiO_2@MPTS and MMIPs nanoparticles were composed of Fe_3O_4, and the Fe_3O_4 nanoparticles remained unchanged after each functionalization step (no decomposition or converting to Fe_2O_3).

FT-IR spectra of Fe_3O_4, Fe_3O_4@SiO_2, Fe_3O_4@SiO_2@MPTS, leached MMIPs, and magnetic non imprinted polymer (MNIPs) were recorded and results ensure further preparation of the MMIPs.

As shown in Figure 2S (ESM), the bands at 590 cm^{-1} are indicative of the presence of the Fe-O-Fe bond. The Fe-O-Fe bond found in Fe_3O_4@SiO_2, Fe_3O_4@SiO_2@MPTS, MMIPs, and MNIPs proved that Fe_3O_4 was embedded in these materials. The peaks around 960 and 1150 cm^{-1} are attributed to the stretching vibration of Si-O-H and Si-O-Si, respectively. The Fe_3O_4@SiO_2@MPTS displayed stretching vibration peak of C=O at 1714 cm^{-1}, suggesting that MPTS was successfully modified onto the surface of Fe_3O_4@SiO_2. Furthermore, the C=O peak of MMIPs and MNIPs at 1730 cm^{-1} showed that they were synthesized through the polymerization of EGDMA and MAA. Thermal analysis graphs of the synthesized $Fe_3O_{4,}$ Fe_3O_4@SiO_2, Fe_3O_4@SiO_2@MPTS and MMIPs magnetic nanoparticles are shown in Figure 3S (ESM). As can be seen in the thermogram of Fe_3O_4@SiO_2@MPTS, the weight loss in the temperature range of 300 to 500 C is about 11.5%, which can be attributed to the loss of MPTS layer. The total weight loss of Fe_3O_4@SiO_2@MPTS@MIP is about 75%, which may be due to the loss of MPTS and imprinted polymer layers. The residue can be associated with the more thermally resistant Fe_3O_4 magnetite particles, giving a magnetite encapsulation efficiency of 25%. The achieved encapsulation efficiency is considerably high and satisfactory. The observations indicate that the synthesis of MMIPs was performed successfully.

Table 1S: Comparison of the DPV responses of the LTG similar compounds at carbon paste electrode (CPE) and magnetic molecular imprinted polymer procedure (MMIP).

Compound	**I (μA)**	
	CPE	MMIP
LTG (1×10^{-7} M)	- 0.49	-15.2
2,4,6-triamino- pyrimidine (1×10^{-7} M)	- 0.41	-1.4
2,6-diamine pyridine (1×10^{-7} M)	- 0.21	-1.7
3-amino-1,2,4-triazine (1×10^{-7} M)	- 0.52	-1.3
2,4-diamino-6-phenyl-1,3,5-triazine (1×10^{-7} M)	- 0.50	-2.1

Table 2S: The effect of time on DPV responses of the LTG by the introduced procedure.

Week	**Added**	**Founded**	**Recovery (%)**
2	100 nM	98.2 nM	98.2
6	100 nM	98.4 nM	98.4
10	100 nM	99.1 nM	99.1
12	100 nM	98.5 nM	98.5
15	100 nM	98.1 nM	98.1
20	100 nM	99.0 nM	99.0
22	100 nM	98.7 nM	98.7
24	100 nM	97.5 nM	97.5
26	100 nM	89.0 nM	89.0
28	100 nM	85.2 nM	85.2

Figure 1S: XRD patterns of synthesized sorbent after each step.

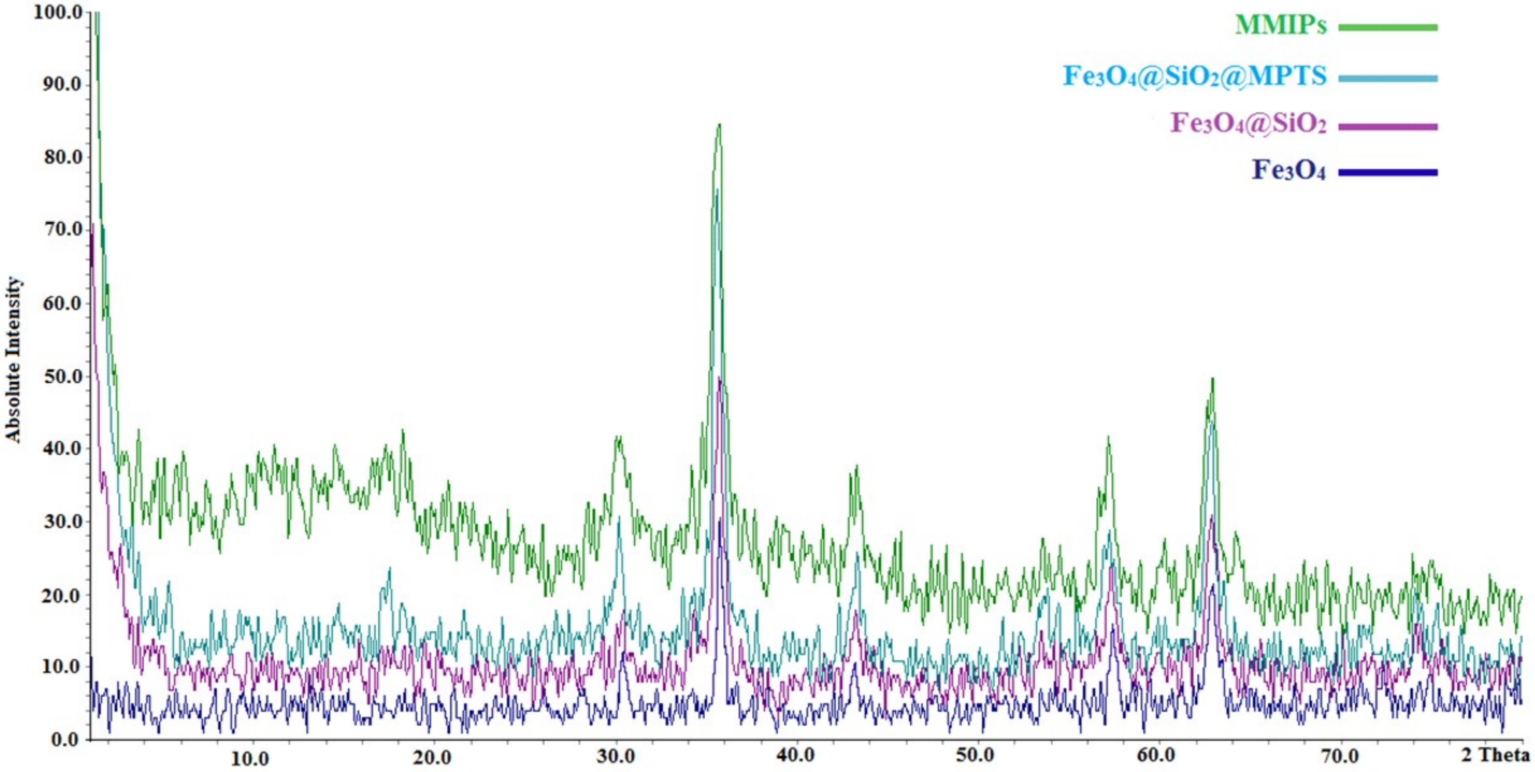


Figure 2S. FT-IR spectra of (a) Fe_3O_4 (b) Fe_3O_4@SiO_2 (c) Fe_3O_4@SiO_2@MPTS (d) Magnetic-MIP (e) Magnetic-NIP.

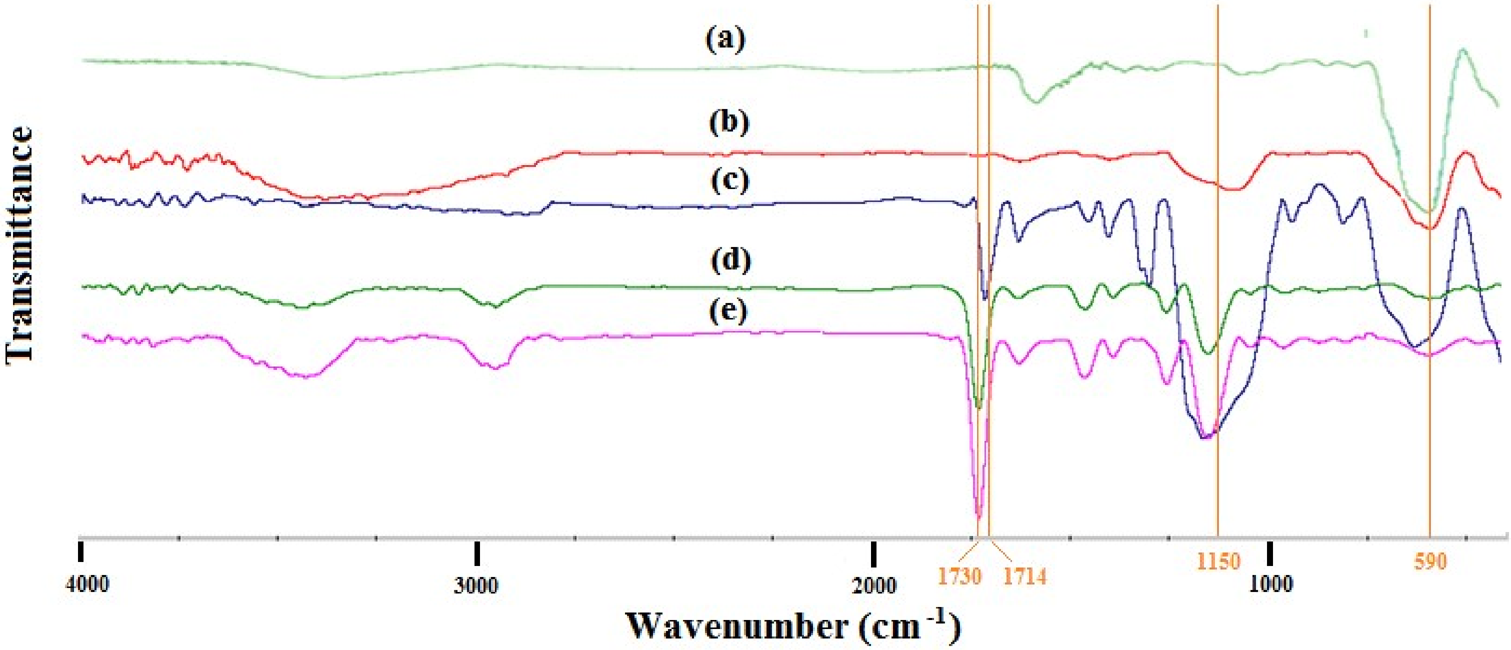
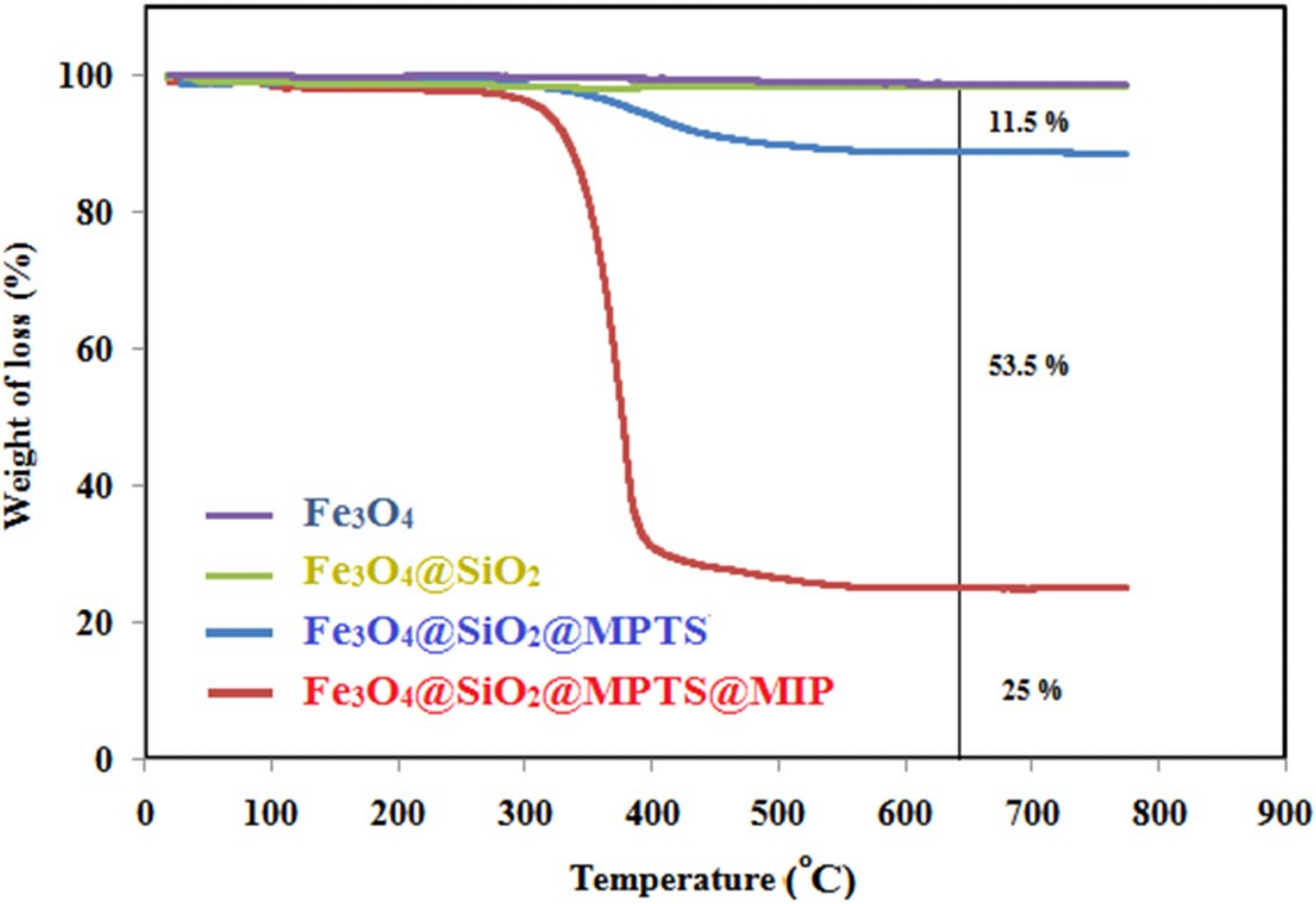


Figure 3S. Thermogravimetric analysis curves of synthesized sorbent after each step.



11.5 %
53.5 %
25 %
Fe3O4
Fe3O4@SiO2
Fe3O4@SiO2@MPTS
Fe3O4@SiO2@MPTS@MIP
Weight of loss (%)
0
20
40
60
80
100
0
100
200
300
400
500
600
700
800
900
Temperature (°C)

Figure 4S. The effect of pH on the LTG extraction by Magnetic-MIP; (a): the DPVs data in different pH, (b): curve of Ip vs pH.

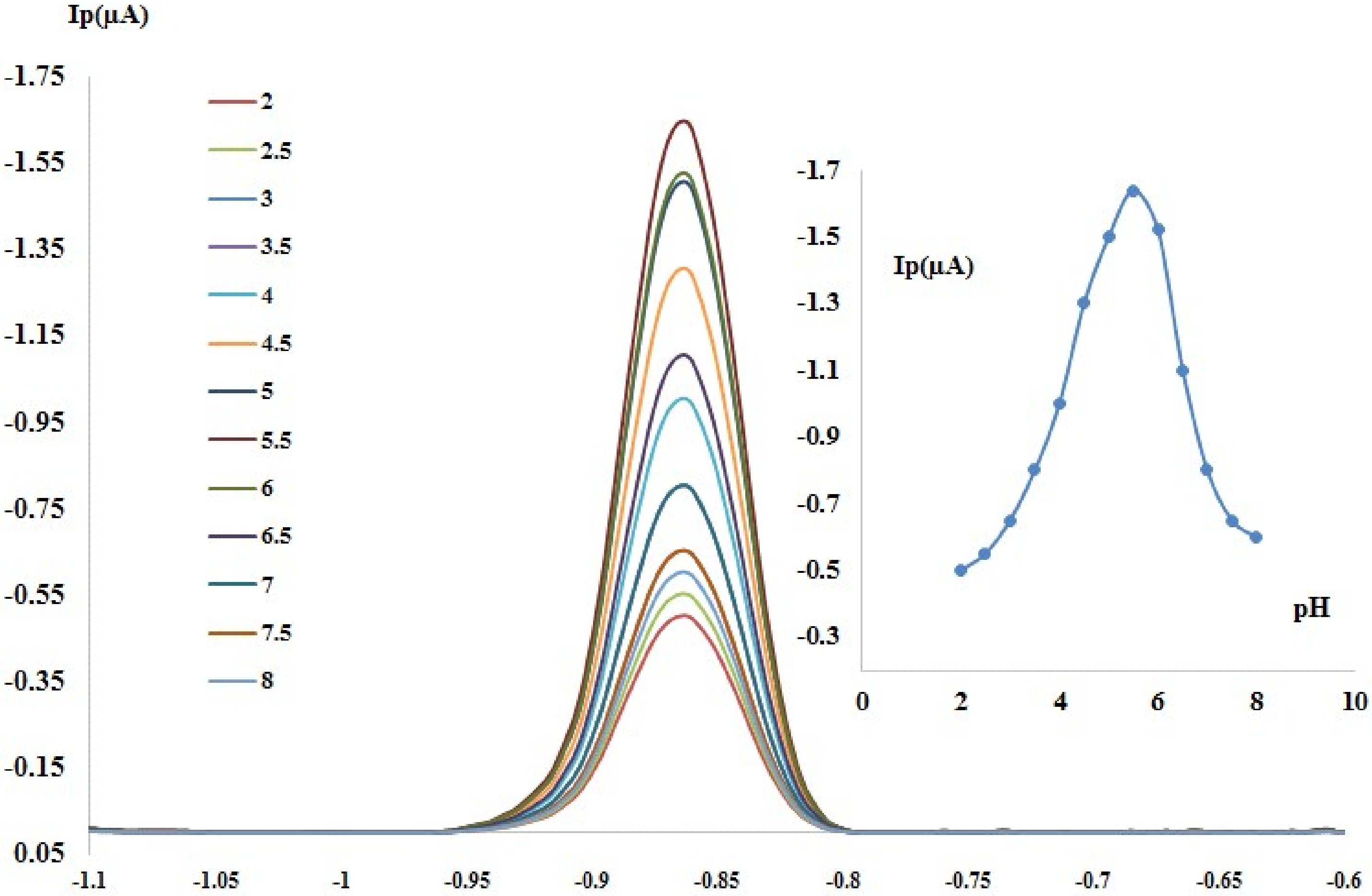


Figure 5S. The effect of extraction time on the differential pulse voltammetric peak current for 1.0 nM LTG.

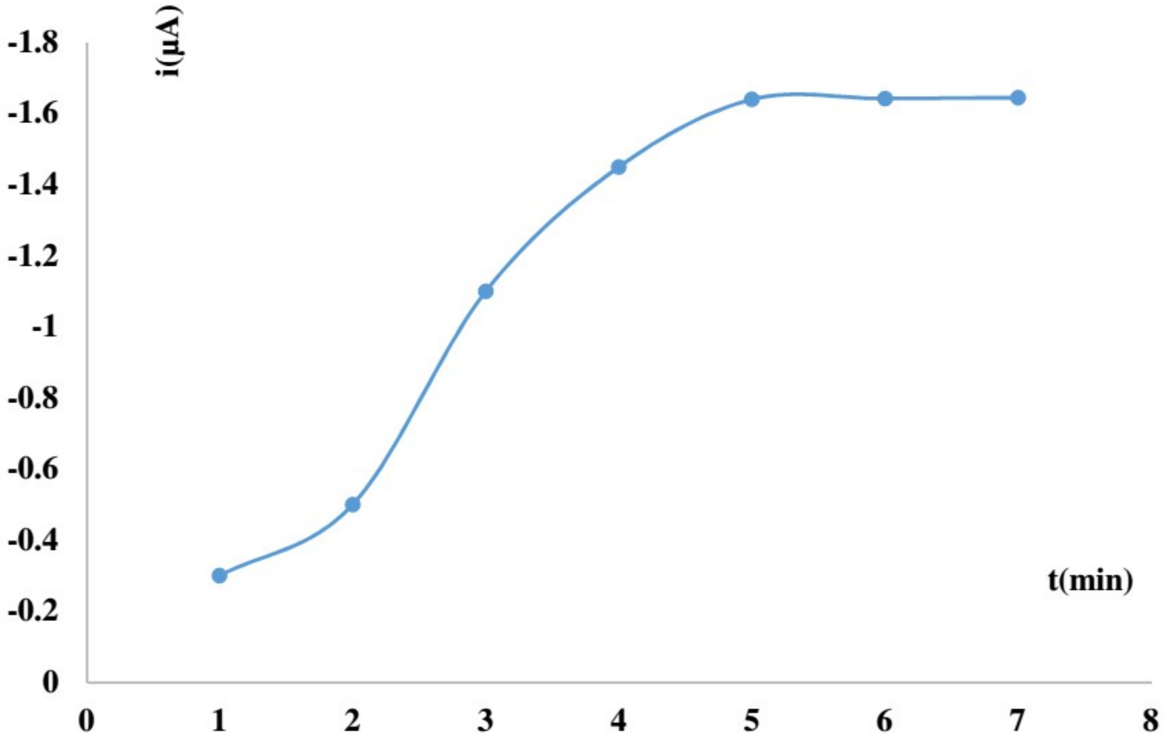
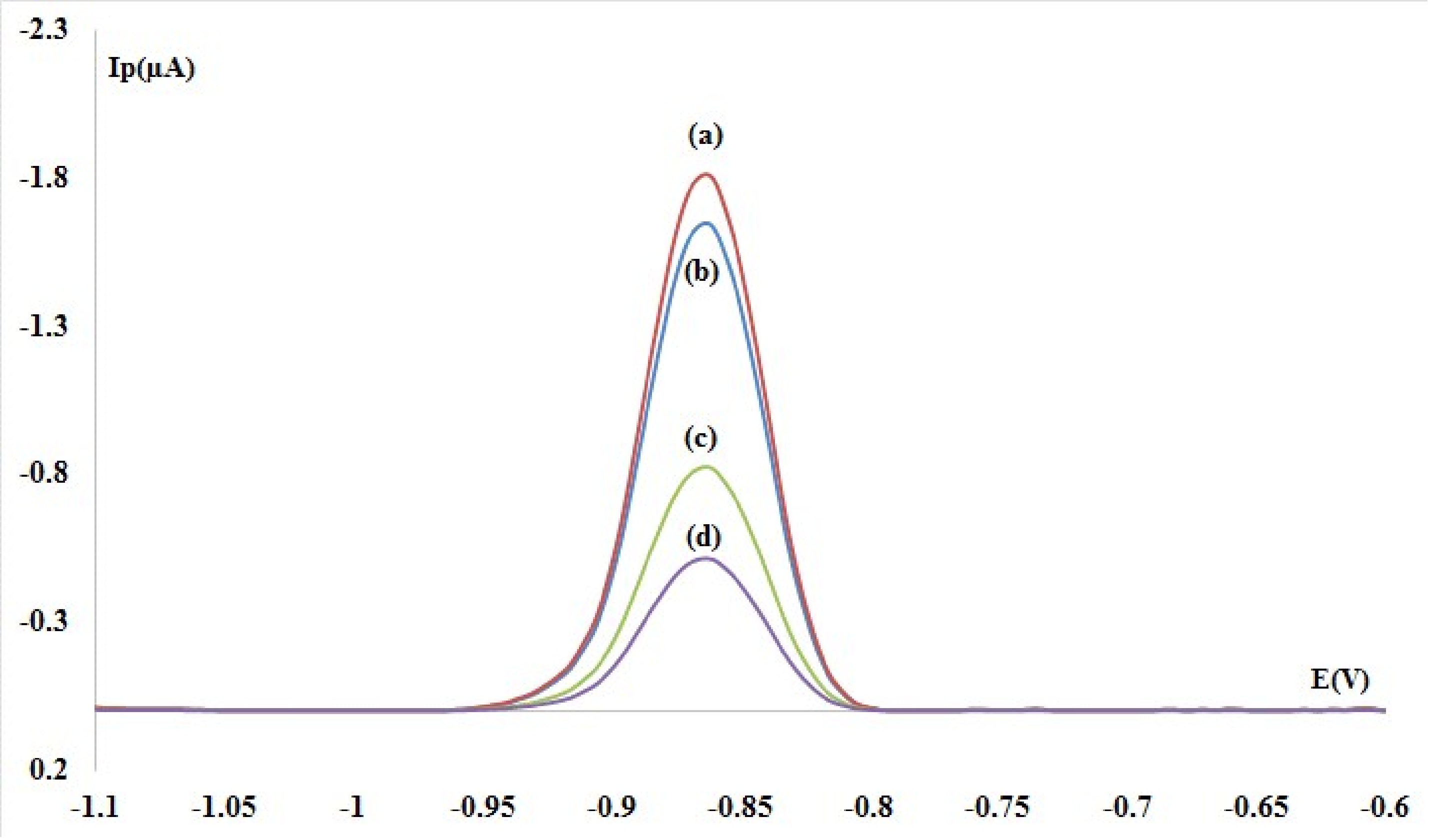


Figure 6S: Comparison of differential pulse voltammetric responses of MC-CPE with magnetic-MIP and magnetic-NIP with and without washing steps; [LTG] = 1.0 × 10 $^{-9}$ M, Solution pH 5.5, shaking time = 5 min, accumulation time = 2 min;(a) Magnetic-MIP before washing (b) Magnetic-MIP after washing with water (c) Magnetic-NIP before washing (d) Magnetic-NIP after washing with water for 30 second.



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